

## REMARKS

Applicant respectfully requests reconsideration in view of the present Amendment. This Amendment is filed in accordance with the Official Gazette notice of 25 February 2003, and the waiver to the requirements set forth under 37 CFR § 1.121 contained therein. Currently in the application, claims 1-19 are cancelled, claims 1-4, 6-10, 12-19 are rewritten and re-presented as new claims 20-36, respectively, and new claims 37-40 are added. Consequently, claims 20-40 are currently pending.

A substitute specification in proper idiomatic English and in compliance with 37 CFR § 1.52(a) and (b) and § 1.125 is supplied as required by the Examiner. Applicant hereby states that the substitute specification contains no new matter. Accompanying the substitute specification is a marked up version of the substitute specification showing all the changes (including the matter being added to and the matter being deleted from) to the specification of record.

A substitute abstract (being of a single paragraph) is supplied as part of the substitute specification. Applicant submits that the substitute abstract is in compliance with MPEP § 608.01(b) and contains no new matter. Notice to that effect is respectfully requested.

Claims 1-19 were objected to and/or rejected over various informalities and under 35 USC § 112. New claims 20-36 are rewritten to address corresponding objections and rejections. Applicant has attempted to comply with all of the suggestions of the Examiner with reference to the amended claims, with the exception of the Examiner's points 6 and 9, as explained below.

With reference to point 6 ("self-cleaning"), Applicant has responded to Examiner's assertion that self-cleaning is not sufficiently qualified by attending to the definition of "self-cleaning" in the specification and by removing the phrase from all of the claims except for claims 33 and 36. Applicant submits that claim 33 is a process claim, and as such, the process itself defines "self-cleaning." With regard to claim 36, "self-cleaning" is defined within claim 36 to "ha[ve] a contact angle of greater than about 150 degrees and an off rolling angle of less than about 1 degree." Applicant submits that the use of the phrase "self-cleaning" is sufficiently clear and definite in claims 33 and 36, and that the rejection under 35 USC § 112 should be withdrawn.

With reference to point 9 ("hydrophobic"), Applicant respectfully traverses the argument that the term "hydrophobic" renders the claim indefinite. While hydrophobic may be used as a relative term, it may also be used in an absolute sense – that is, hydrophobic is not hydrophilic nor is it neutral relative to charged liquid (e.g., water), equally definite is the meaning of hydrophobic as lacking an affinity for water, or tending not to be wetted by water. Any of these non-relative definitions are supported by the specification, are understood by one of ordinary skill in the art and are commonly available dictionary definitions. Thus, even if there is no standard for ascertaining a requisite degree of hydrophobicity, the claim element is satisfied at *any degree* of hydrophobicity. Applicant submits that the use of the word "hydrophobic" is sufficiently clear and definite in the claims, and that the rejection under 35 USC § 112 should be withdrawn.

With particular reference to point 10 by the Examiner regarding glazed or enamelled substrates, the claims have been amended to define generally that the substrate itself may have a glaze or enamel coating on it prior to the application of

the, for example in claim 20, "fired-on coating." That is, the glaze or enamel is defined as part of the substrate, and not as part of the coating on the substrate.

Claims 1-5, 8-11, 16 and 18 were rejected under 35 USC § 102(b) as being anticipated by Shouji. Claim 1 is rewritten as claim 20 to define "a fired-on coating disposed on a surface of the substrate." Support for a fired-on coating is found at least in Example 1 of the specification as filed. Shouji does not disclose "a fired-on coating," rather Shouji discloses only an organic polymer coating formed by the curing or polymerization of monomers (with or without a heat-cure step, which is different from a firing step). Thus, Shouji does not disclose, teach or suggest the invention as defined in claim 20, and claim 20 is allowable over the art of record. Notice to that effect is respectfully requested.

Claims 21-23 depend from allowable claim 20 and define further features of the invention. It is axiomatic that a claim that depends from an allowable claim is also allowable. Accordingly, Applicant submits that claims 21-23 are also allowable. Notice to that effect is respectfully requested.

With reference to claim 6, claim 6 is rewritten as claim 24 and defines a layer forming material of a coating that is a "glass or a material which forms Me-O-Me' structural elements." Support is found in the original specification starting at the bottom of page 4. As stated hereinabove, Shouji discloses only an organic polymer as a binder, Shouji does not disclose, teach or suggest a layer-forming material as defined in claim 24. Accordingly, the rejection to claim 24 under 35 USC § 102(b) should be withdrawn. Notice to that effect is respectfully requested.

Claim 7 was not rejected based on the art references of record. Claim 7 is rewritten in independent form as new claim 25 to address the objections/rejections based on informalities and under 35 USC § 112. Applicant submits that claim 25

overcomes the objections and rejections based on informalities and 35 USC § 112 and, because there was no rejection based on the art references of record, is therefore in condition for allowance. Notice to that effect is respectfully requested.

Claims 8-10 were rewritten as claims 26-28, respectively, to address objections and rejections based on informalities and 35 USC § 112. Claims 26-28 depend from allowable claim 25 and define further features of the invention, and are thus also allowable.

Claim 12 was not rejected based on the art references of record. Claim 12 is rewritten as new claim 29 to address the objections and rejections based on informalities and 35 USC § 112. As there were no rejections based on the art, Applicant submits that new claim 29 is in condition for allowance and notice to that effect is respectfully requested.

Claims 13-15 define further features of the invention and were rewritten as claims 30-32 to address objections and rejections based on informalities and 35 USC § 112. Claims 30-32 depend from allowable claim 29, and are thus also allowable.

Claim 16 was rejected under 35 USC § 112 as being anticipated by Shouji. Claim 16 is rewritten as claim 33 to address the objections and rejections based on informalities and 35 USC § 112. Claim 33 defines "firing the composition to form a cohesive layer." Shouji discloses a polymeric coating material that forms a film by polymerization, not by firing. Shouji does not disclose, teach or suggest a step of forming a cohesive layer by firing. Accordingly, the rejection under section 102 is overcome and claim 33 is allowable over the art of record. Notice to that effect is respectfully requested.

Claim 17 was not rejected based on the art references of record. Claim 17 was rewritten as claim 34 to address the objections and rejections based on informalities and 35 USC § 112. As there were no rejections based on the art, Applicant submits that claim 34 is in condition for allowance and notice to that effect is respectfully requested.

Claim 18 was rejected under 35 USC § 112 as being anticipated by Shouji. Claim 18 is rewritten as claim 35 to address the objections and rejections based on informalities and 35 USC § 112. Claim 35 depends from allowable claim 33. As noted hereinabove, a claim that depends from an allowable claim is also allowable.

Claim 19 was not rejected based on the art references of record. Claim 19 is cancelled and rewritten as new claim 36 to address the Examiners' concerns stated in point 20 of the office action and to address the objections and rejections based on informalities and 35 USC § 112. That is, new claim 20 is no longer in a method/process form. As there were no rejections based on the art, Applicant submits that claim 36 is in condition for allowance and notice to that effect is respectfully requested.

New claims 37-40 are added to define further features of the invention. In particular, the art of record does not disclose, teach or suggest "a vitreous binder that responds to firing by affixing the plurality of nanoscale particles to the substrate surface" as defined in claim 37, and claims 38-40 depend from claim 37. Applicant submits that new claims 37-40 are in condition for allowance, and allowance thereof is respectfully requested.

In light of the foregoing, it is respectfully submitted that the present Application is in a condition for allowance and notice to that effect is hereby

requested. If it is determined that the Application is not in a condition for allowance, the Examiner is invited to initiate a telephone interview with the undersigned to expedite prosecution of the Application.

A supplemental information disclosure statement is filed herewith in compliance with 37 CFR § 1.56. Accompanying the supplemental information disclosure statement is a statement containing concise explanations of the relevance of corresponding foreign language references.

If there are any additional fees resulting from this communication, please charge the same to our Deposit Account No. 18-0160, our Order No. FER-12790.

Respectfully submitted,  
RANKIN, HILL, PORTER & CLARK LLP



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SUBSTRATES WITH A SELF-CLEANING SURFACE, A PROCESS FOR THEIR

PRODUCTION AND THEIR USE

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RECEIVED  
AUG 28 2003  
TC 1700

RECEIVED  
AUG 14 2003  
TC 1700

1. REFERENCE TO RELATED APPLICATIONS

This application is the National Stage of International Application No. PCT/WO/02/49980, filed December 4, 2001, which claims priority to German Application DE 100 63739.6 filed December 21, 2000, the disclosures of which are hereby incorporated by reference in their entirety.

Description 2. TECHNICAL FIELD

The invention relates to a substrate with at least one self-cleaning surface, ~~the substrates being in particular a substrate of~~ is preferably a glass, ceramic, plastic or metal substrate, or a glazed or enamelled coated substrate. The self-cleaning surface located on the substrate is based on a coating ~~with structure-forming particles which is located on the substrate, resulting in the coating forming a structure, and the surface structure of~~ configured to have elevations and depressions; depressions. Further, the surface is at least partly hydrophobic. The invention also relates to a composition for the production of a substrate ~~according to the invention with at least one self-cleaning surface. The invention also relates to~~ surface, and to a process for the production of the substrate with at least one self-cleaning surface, which comprises same. The process includes coating the substrate with the abovementioned composition. Finally, ~~the composition or coating. The invention also relates to the use of the substrates according to the invention with various uses of a substrate having a self-cleaning surface.~~

### 3. DESCRIPTION OF RELATED ART

~~It is known that to achieve~~To achieve both a good self-cleaning effect on a surface, ~~in addition to a good~~surface having a good level of hydrophobicity ~~this must also have a micro rough surface structure.~~there must be a micro rough surface structure on the surface of a substrate. Both features (micro rough and hydrophobicity) are realized in nature, for example, in the lotus leaf. ~~The surface~~example in the lotus leaf; ~~the surface form from~~of the lotus leaf has a hydrophobic material~~has pyramid shaped elevations a few  $\mu$ m from one another.~~Drops of water come into contact substantially only with these peaks,and pyramid shaped elevations that are a few  $\mu$ m from one pyramid tip to another pyramid tip. Drops of water substantially contact only with the tips or peaks of the pyramids so that the contact area of water to surface is minuscule relative to the water ~~is minuscule, resulting in a very low adhesion.~~ These relationships ~~and the main~~drops contacting a micro smooth surface. The reduced surface area results in a very low adhesion between the water drops and the micro rough surface. The relationship of micro rough surfaces and hydrophobicity, and the applicability of the "lotus effect" to technical surfaces are the doctrine of "lotus effect" on surfaces, is taught by A.A. Abramzon, Khimia i Zhizu (1982), no. 11, 38-40:38 40.

~~Without reference to the lotus effect, US 3, 354,022 discloses water repellent surfaces, the surface having a micro rough structure with elevations and depressions and being formed from a hydrophobic material, in particular a fluorine containing polymer. According to one embodiment, a surface with a self cleaning effect can be applied to ceramic brick or to glass by coating the substrate with a suspension which~~



~~comprises glass beads with a diameter in the range from 3 to 12  $\mu$ m and a fluorocarbon wax based on a fluoroalkyl ethoxymethacrylate polymer. Their low abrasion resistance and moderate self-cleaning effect are a disadvantage of such coatings. LOTUS EFFECT<sup>®</sup>, U.S. Patent No. 3,354,022 discloses water repellent surfaces having a micro rough structure with elevations and depressions and a hydrophobic material. In particular, a fluorine containing polymer is disclosed as the hydrophobic material. According to one embodiment, a surface with a self-cleaning effect can be applied to ceramic brick or glass by coating the substrate with a suspension comprising glass beads and a fluorocarbon wax. The beads have a diameter in the range from 3 to 12  $\mu$ m. The fluorocarbon wax is a fluoroalkyl ethoxymethacrylate polymer. Unfortunately, such coatings have a disadvantageously low abrasion resistance and only a moderate self-cleaning effect.~~

~~The doctrine of EP 0 909 747 A1 is a process for producing a self-cleaning property of surfaces, in particular roof tiles. The surface has hydrophobic elevations with a height of 5 to 200  $\mu$ m. Such a surface is produced by application of a dispersion of powder particles of an inert material in a siloxane solution and subsequent curing. As in the process acknowledged above, the structure-forming particles are not fixed on the surface of the substrate in an abrasion-stable manner.~~

European Patent No. EP 0 909 747 A1 discloses a process for producing a self-cleaning property of a surface. The method relates particularly to the surface of roof tiles. The surface has hydrophobic elevations having a height of 5 to 200  $\mu$ m. Such a surface is produced by application of a dispersion of powder particles of an inert material in a siloxane solution, and subsequent curing the siloxane solution to form a

polysiloxane. Unfortunately, the structure forming particles are not well fixed to the surface of the substrate in an abrasion stable manner and thus the abrasion resistance is undesirably low.

~~The doctrine of EP Patent 0 772 514 is self cleaning surfaces of objects with a synthetic surface structure of elevations and depressions, the distance between the elevations being in the range from 5 to 200  $\mu\text{m}$  and the height of the elevations being in the range from 5 to 100  $\mu\text{m}$  and the structure comprising hydrophobic polymers or materials which have been hydrophobized in a stable manner. Etching and embossing processes, and furthermore coating processes are suitable for formation of the structures. If necessary, the formation of the structure is followed by a hydrophobization, for example a so called silanization.~~

European Patent No. EP 0 772 514 discloses a self-cleaning surface for objects with a synthetic surface structure having elevations and depressions. The distance between the elevations is in the range of from 5 to 200  $\mu\text{m}$ , and the height of the elevations is in the range from 5 to 100  $\mu\text{m}$ . The structure includes hydrophobic polymers, or materials that have been hydrophobized in a stable manner. Etching, embossing, and coating processes are suitable to form the structure. If necessary, the formation of the structure can be followed by a hydrophobization step, for example a silanization process.

~~Similarly structured surfaces with hydrophobic properties are the doctrine of EP 0 933 388 A2. The surface has elevations with an average height of 50 nm to 10  $\mu\text{m}$  and an average separation of between 50 nm to 10  $\mu\text{m}$ , and a surface energy of the non-structured material of 10 to 20 mN/m. To achieve a particularly low surface energy and~~

~~thus hydrophobic and oleophobic properties, the structured surface comprises fluorine-containing polymers or has been treated using alkylfluorosilanes. Indications of also using coating processes, instead of the shaping processes disclosed here, for structuring the surface are not to be obtained from this document.~~

Structured surfaces with hydrophobic properties are disclosed in European Patent No. EP 0 933 388 A2. The surfaces have elevations with an average height of 50 nm to 10  $\mu$ m and an average separation of between 50 nanometers (nm) to 10 micrometers ( $\mu$ m), and a surface energy of the non structured material of 10 to 20 micronewtons per meter (mN/m). To achieve a particularly low surface energy, and thus hydrophobic and oleophobic properties, the structured surface includes fluorine containing polymers or has been treated using alkylfluorosilanes.

~~The doctrine of DE Patent Application 100 16 485.4 is glass, ceramic and metal substrates with a self-cleaning surface based on a structured and at least partly hydrophobized coating. The coating comprises a glass flux and structure-forming particles with an average particle diameter in the range from 0.1 to 50  $\mu$ m. The glass flux and structure-forming particles are present in a volume ratio in the range from 0.1 to 5 and the micro-rough surface structure has a ratio of average profile height to average distance between adjacent profile peaks in the range from 0.3 to 10. The self-cleaning surface has a higher abrasion resistance than self-cleaning surfaces of roof tiles according to the EP 0 909 747 A1 acknowledged above.~~

German (DE) Patent Application 100 16 485.4 discloses glass, ceramic and metal substrates having a self-cleaning surface. The surface has a structured and at least partly hydrophobized coating. The coating includes a glass flux and structure

forming particles with an average particle diameter in the range from 0.1 micrometers ( $\mu\text{m}$ ) to 50 micrometers ( $\mu\text{m}$ ). The glass flux and structure forming particles are present in a volume ratio in the range from 0.1 to 5. The micro rough surface structure has a ratio of average profile height to average distance between adjacent profile peaks in the range from 0.3 to 10. The self-cleaning surface has a higher abrasion resistance relative to the self-cleaning surfaces of roof tiles disclosed hereinabove.

~~The object of the invention is to provide substrates, in particular substrates of glass, ceramic, plastic and metal and glazed and enamelled substrates, with at least one self-cleaning surface which not only have a low roll-off angle or high contact angle and therefore a good self-cleaning effect, but furthermore are transparent. The self-cleaning surface should have a very high contact angle with respect to water, preferably a contact angle of about/above  $150^\circ$ . The transparency of a transparent substrate, such as glass or plastic, should as far as possible not be reduced. A decoration under the self-cleaning surface should remain clearly detectable. According to a further object, glass, ceramic or metal substrates or glazed or enamelled substrates according to the invention should have a higher abrasion resistance than substrates which are already known and on which the structured surface is made of an organic polymer or comprises structure-forming particles bonded in an organic~~

### SUMMARY OF THE INVENTION

The present invention provides a substrate, and preferably a glass, ceramic, plastic, metal and/or glazed or enamelled substrate, with a self-cleaning surface. The

self-cleaning surface preferably has a low roll off angle or high contact angle (and therefore a good self-cleaning effect), and is also transparent. The self-cleaning surface preferably has a very high contact angle with respect to water, preferably a contact angle of about/above 150°.

Subjecting the substrate to a hydrophobating process according to the present invention preferably does not reduce the transparency of a transparent substrate, such as glass or plastic. Additionally, a decorated surface subjected to a hydrophobating process according to the present invention, where the decoration is under the self-cleaning surface, is preferably clearly detectable by an observer of the surface. Glass, ceramic, and metal substrates, or glazed or enamelled substrates, preferably have a higher abrasion resistance relative to known hydrophobic substrates, in particular with reference to a structured surface that is made of an organic polymer, or that includes structure-forming particles bonded using an organic polymeric material. Additionally, the substrates with the self-cleaning surface according to the invention are preferably formed using a simple polymeric material. According to a further object of the invention, the substrates with the self-cleaning surface according to the invention should be obtainable by means of a simple process, preferably by processes such as are used in the glass and ceramics industry or metal processing process. A preferred process is similar to processes used in the glass and ceramics industry or metal processing industry for decorating surfaces. These and further objects such as are deduced from the further description do not have to be achieved together in all the embodiments.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

~~The invention accordingly provides a substrate, in particular a substrate of present invention provides a self-cleaning or hydrophobic coated substrate. The substrate is preferably glass, ceramic, plastic and metal or metal, or is a glazed or enamelled coated substrate, and has a self-cleaning or hydrophobic coating arranged thereon. The coating includes particles substrate, with at least one self-cleaning surface, comprising a coating which is arranged on the substrate, comprises particles which that form a surface structure and on the coating opposite the coating side that contacts the substrate. The coating is at least partly superficially hydrophobic. The structure forming particles preferably have an average diameter of less than 100 nanometers (nm).~~

~~Substrates according to the invention, having a "nanoscale" structured surface and a superficially hydrophobic coating thereon, have an outstanding self-cleaning effect hydrophobic, which is characterized in that when the structure-forming particles have an average diameter of less than 100 nm. The subclaims relate to nanometers (nm). A preferred embodiment, particle diameter is preferably in the range from 5 nm to 50 nm.~~

~~It has been found that substrates with a superficially hydrophobic coating with a "nanoscale" surface structure have an outstanding self-cleaning effect if the coating comprises structure-forming particles with an average diameter of less than 100 nm. The particle diameter is preferably in the range from less than 50 nm to 5 nm. The term average diameter here is understood as meaning the diameter of primary particles, and not the diameter of agglomerates. In general, at least 90 % and preferably about~~

~~100 % of the primary particles have a diameter of less than 100 nm and particularly preferably less than 50 nm. The term "nanoscale" means that the structure has considerably lower profile heights and distances between profile peaks—apart from in agglomerates these are smaller than the particle diameter than surfaces with structure-forming particles in the micrometre range.~~

The term "average diameter" as used herein is the diameter of primary particles, and is not the diameter of agglomerates. In general, at least 90 % and preferably about 100 % of the primary particles have a diameter of less than 100 nm and particularly preferably less than 50 nm. The term "nanoscale" means that the structure has considerably lower profile heights and distances between profile peaks than surfaces with structure forming particles in the micrometer range (i.e., "microscale").

~~The structure-forming particles can be organic or inorganic substances. Examples of the inorganic substances which may be mentioned are: metal oxides, mixed oxides, silicates, sulfates, phosphates, borates, metal sulfides, oxosulfides, selenides and sulfoselenides, metal nitrides and oxide-nitrides and metal powders. Examples of the organic structure-forming particles which may be mentioned are carbon blacks and nanoscale organic polymeric particles, and among these fluorine-containing polymers. Many structure-forming particles with the particle diameter according to the claims, such as, in particular, 5 to less than 50 nm, are commercially obtainable. They can otherwise be obtained by precipitation processes which are known per se or by pyrogenic processes, gaseous starting substances being converted into pulverulent substances. The structure-forming particles are particularly preferably metal oxides from the series consisting of silica ( $\text{SiO}_2$ ), titanium dioxide ( $\text{TiO}_2$ ), aluminium oxide ( $\text{Al}_2\text{O}_3$ ),~~

~~zirconium dioxide ( $\text{ZrO}_2$ ) and tin dioxide ( $\text{SnO}_2$ ). These oxides are particularly preferably pyrogenically prepared oxides, and among these in particular silica. Pyrogenic silicas are commercially obtainable with an average primary particle size in the range from about 7 to 40 nm.~~

The structure forming particles can be either organic or inorganic substances. Examples of suitable inorganic structure forming particles are: metal oxides, mixed oxides, silicates, sulfates, phosphates, borates, metal sulfides, oxosulfides, selenides and sulfoselenides, metal nitrides and oxide nitrides and metal powders. Examples of suitable organic structure forming particles are: carbon blacks, nanoscale organic polymeric particles, and nanoscale organic polymeric particles containing fluorine. Structure forming particles having a particle diameter according to the invention are commercially available, otherwise the particles can be obtained by precipitation processes which are known, for example, by pyrogenic processes, and by gaseous starting substances that are converted into pulverulent substances.

The structure forming particles are preferably metal oxides selected from the series consisting of silica ( $\text{SiO}_2$ ), titanium dioxide ( $\text{TiO}_2$ ), aluminium oxide ( $\text{Al}_2\text{O}_3$ ), zirconium dioxide ( $\text{ZrO}_2$ ) and tin dioxide ( $\text{SnO}_2$ ). These oxides are preferably pyrogenically prepared oxides, and among these silica is most preferred. Pyrogenic silica with an average primary particle size in the range from about 7 nm to 40 nm is commercially available.

~~In addition to the structure-forming particles, the self-cleaning surface of substrates according to the invention comprises a layer-forming material, which can be an inorganic or organic material. The layer-forming material either forms a~~



~~homogeneous layer in which the structure-forming particles are fixed in the form of their primary particles and/or agglomerates, or the structure-forming particles are fixed on the substrate by means of the layer-forming material. Some of the primary particles and/or agglomerates thereof project at least partly out of the surface and in this manner form elevations and depressions, which, in addition to the hydrophobization, are responsible for the effect according to the invention.~~

As disclosed hereinabove, the self-cleaning substrate surface according to the invention includes a coating or layer forming material. And, the coating can be an inorganic or organic material. The coating can be a homogeneous layer over the structure forming particles where the primary particles and/or agglomerates are fixed to the substrate surface, or the particles are incorporated into the coating, which affixes the particles to the substrate surface (that is, the coating is the particles' binder). Some of the primary particles and/or agglomerates thereof project at least partly out of the coating surface to form elevations and depressions, which, in addition to the hydrophobization coating, are responsible for the self-cleaning effect according to the invention.

~~Among the layer-forming materials, inorganic materials are particularly preferred. The material is expediently a vitreous material. Such a material can have been formed in the context of ceramic firing from one or more glass frits or glass-forming raw materials. During the firing, the vitreous material encloses structure-forming particles such that some of these project out of the surface. The glass frits employed for the production of the self-cleaning surface according to the invention are those with a~~

~~composition which has a melting point below that of the structure forming particles and below the deformation temperature of the substrate to be coated.~~

A preferred coating includes an inorganic material, preferably a vitreous inorganic material. The coating is formed by a ceramic firing process performed on one or more glass frits or glass forming raw materials. That is, glass frit is used that has a melt point that is lower relative to the substrate and the structure forming particles. That is, the glass frit has a melting point below that of the structure forming particles and below the deformation temperature of the substrate to be coated.

During the firing, the temperature is increased to above the melt point of the glass frit, but below the melt point of the substrate and the structure forming particles. The vitreous material melts and flows to enclose the structure forming particles and affix the particles to the surface of the substrate. Some of the particles project away from the surface out of the molten glass frit. The glass frit cools to harden and bind the structure forming particles to the substrate surface.

~~According to an alternative embodiment, the vitreous material is a substance which, during firing from one or more glass-forming raw materials, in particular low-melting oxide or sufficiently reactive raw materials, forms vitreous bonds with constituents of the substrate and/or some of the structure-forming particles. These bonds are structural elements of the general formula  $\text{Me-O-Me'}$ , wherein Me and Me' can be identical or different and represent boron, silicon, phosphorus, aluminium, titanium, tin, zirconium or other metals of the substrate.~~

Rather than glass frit, alternatively the vitreous material is a glass-forming material that forms vitreous bonds with constituents of the substrate and/or some of the

structure forming particles during a firing process. In particular, low melting oxidic or sufficiently reactive raw materials can be so used. The vitreous bonds are structural elements of the general formula Me-O-Me', wherein Me and Me' are generally metals and can be identical or different from each other. Me and Me' are selected from the group consisting of boron, silicon, phosphorus, aluminium, titanium, tin, zirconium and other metals suitable as a substrate.

~~An example of a material which contains Me-O-Me' structural elements and in which the structure forming particles are embedded is a system such as is obtained, during firing carried out after coating, by coating glass or a vitreous or enamelled substrate with a composition comprising boric acid and/or an alkali metal phosphate and structure forming particles. The boric acid and/or the phosphate thus form a chemical bond to reactive groups of the glass substrate or the glazing/enamel layer and optionally additionally the structure forming particles during the firing.~~

An example of a material which contains Me-O-Me' structural elements and in which the structure forming particles are embedded is a system obtained during a firing of a coating glass or a vitreous or enamelled substrate with a composition comprising boric acid and/or an alkali metal phosphate and structure forming particles. The boric acid and/or the phosphate form a chemical bond to reactive groups of the glass substrate or the glazing/enamel layer and may also bond with the structure forming particles during the firing.

~~According to a further alternative, coating materials with Me-O-Me' structural elements are those systems such as are formed from organometallic compounds of the~~

~~elements boron, silicon, aluminium, titanium and zirconium which have at least two hydrolysable groupings during alcoholysis/hydrolysis with a subsequent condensation reaction and optionally subsequent firing.~~

Alternatively, coating materials with Me-O-Me' structural elements include systems formed from organometallic compounds of the elements boron, silicon, aluminium, titanium and zirconium, where the system has at least two hydrolysable groups available for alcoholysis/hydrolysis with a subsequent condensation reaction, and an optional subsequent firing.

~~According to a preferred embodiment of the substrate according to the invention with a self-cleaning surface, the structured coating comprises structure-forming particles with an average diameter of less than 100 nm, in particular in the range from 5 nm to less than 50 nm, and a layer-forming inorganic or organic material in a weight ratio in the range from 100 : 1 to 1 : 2, in particular 20 : 1 to 1 : 1. A ratio outside the limits mentioned is indeed possible, but if the content of layer-forming material is too low, a possibly inadequate fixing of the structure-forming particles is the consequence. In the case of too high a content of the layer-forming material, the self-cleaning effect decreases because the structure-forming particles may be sunk too low in the layer-forming material.~~

In another embodiment, a coating having a surface structure according to the invention includes structure forming particles with an average diameter of less than 100 nm, and preferably in the range from about 5 nm to less than about 50 nm, and a layer forming inorganic or organic material in a weight ratio in the range from 100 : 1 to 1 : 2, in particular 20 : 1 to 1 : 1. While a ratio outside the above parameters is possible, it is

believed that the content of layer forming material would be too low, and would possibly be inadequate to affix the structure forming particles to the substrate. If there is too much layer forming material, it is believed that the self-cleaning effect would decrease because the structure forming particles would be sunk too low in the layer forming material, and would not protrude sufficiently to create the desired elevations and depressions.

~~Preferred substrates have a coating which substantially comprises structure-forming particles and a layer-forming inorganic material, but the coating can additionally comprise adhesion promoters or these compounds such as are formed from auxiliary substances present and/or precursors of the layer-forming material during the production of the coating, including a heat treatment step which may be necessary or firing.~~

A preferred substrate has a coating that includes structure forming particles and a coating formed of a layer forming inorganic material. The coating can further include adhesion promoters or compounds formed from auxiliary substances present and/or precursors of the layer forming material during the production of the coating. The coating production process can include a heat treatment step, which may be necessary for firing.

~~In order to impart to the structured surface the necessary hydrophobic properties and also the desired high contact angle, in particular about/above 150°, or low roll off angle, in particular about/below 1°, there is on the structured layer as a rule a hydrophobic layer, for example one such as is obtained by silanization.~~

In order to impart to the structured surface the necessary hydrophobic properties, and thus create the desired high contact angle and/or low roll off angle, a hydrophobic layer is disposed on the structured substrate surface or layer. For example, a suitable hydrophobic layer can be obtained by silanization. In particular, a desirable contact angle is above about 150°, and a desirable low roll off angle is below about 1°. The phrase "self-cleaning" is generally synonymous with a contact angle or a low roll off angle in the above-described preferred range.

~~According to a further embodiment, the self-cleaning surface according to the invention also comprises, in addition to the nanoscale elevations and depressions produced by the structure-forming particles, an over-structure, elevations and depressions in regular or stochastic distribution forming a micro-rough structure. The term "micro-rough" means a height of the profile peaks and a distance between the profile peaks in the range from 0.1 to 50 µm, in particular 0.5 to 15 µm. Such substrates according to the invention with a nanoscale and additionally a microscale surface roughness can have a single or two structure-forming coatings on the substrate, in the first case the nanoscale and microscale particles being distributed in a layer-forming material. In the second case there is a coating with the nanoscale particles on a coating with the microscale particles which has been applied beforehand.~~

~~According to a particularly preferred embodiment, the substrate is a glass or an enamelled glass, the coating according to the invention to achieve the self-cleaning properties being substantially transparent.~~

In another embodiment according to the invention, a microscale over structure forming a micro rough surface is formed on a substrate surface. A nanoscale rough

surface is then formed onto the microscale over structure, and the surface is then hydrophobized. The over structure forms elevations and depressions in a regular or stochastic (random) distribution over the self-cleaning surface of the substrate. "Micro rough" is preferably a height of the profile peaks in a range from 0.1 micrometers ( $\mu\text{m}$ ) to 50  $\mu\text{m}$  and a distance between the profile peaks in a range from 0.1 micrometers ( $\mu\text{m}$ ) to 50  $\mu\text{m}$ , and preferably a height and distance in a range of 0.5  $\mu\text{m}$  to 15  $\mu\text{m}$ .

Substrates according to the invention having a nanoscale structure over a microscale structure can have either one or two structure forming coatings on the substrate. In a single coating, the nanoscale and microscale particles are distributed in the same coating. In a two coating system, there is a first coating with microscale particles that is applied to the substrate, and subsequently a second coating with nanoscale particles is applied to the substrate having the microscale particles already affixed thereto.

~~Substrates according to the invention with a self-cleaning surface have a superficially hydrophobic coating. If the coating itself does not have hydrophobic properties, this property is effected by application of a substance having a hydrophobizing action to the structured surface. Organosilanes, and here in particular fluorine-containing organosilanes, are particularly expedient for the hydrophobization. If the coating material of the structure-forming surface is a vitreous material, Si-O-Si structural elements can also be formed by using organosilanes having a hydrophobizing action, as a result of which the component having a hydrophobizing action is fixed firmly to the structured substrate and the self-cleaning properties thus remains [sic] permanently.~~

With further reference to the hydrophobic coating according to the invention, the coating itself may not have inherent hydrophobic properties, for example when the coating is used as a binder for the structure forming particles rather than a hydrophobic overcoat. If the coating is not inherently hydrophobic, the hydrophobicity is effected by applying a hydrophobizing substance to the structured surface. Suitable hydrophobizing substances include organosilanes, and in particular fluorine containing organosilanes. If the coating, acting as a binder, is a vitreous material, then using organosilanes having a hydrophobizing action can form Si-O-Si structural elements. As a result, the hydrophobizing substance is fixed firmly to the structured substrate via the Si-O-Si bonds to form a permanent self-cleaning property.

~~The invention furthermore relates to the process for the production of substrates according to the invention and to compositions such as are used in the production thereof.~~

The present invention relates to compositions suitable to for use in forming self-cleaning surfaces, and to processes for the production of substrates having self-cleaning surfaces using the compositions.

~~The compositions for the production of a substrate according to the invention with a self-cleaning surface are substance mixtures which comprise structure-forming particles with an average particle diameter of less than 100 nm, in particular particles with an average particle diameter in the range from 5 nm to less than 50 nm, and a layer-forming particulate or liquid material. As mentioned above, the particle diameter is that of the primary particles and the diameter of at least 90 %, preferably substantially of all the particles, is preferably less than 100 nm, or less than 50 nm.~~



The compositions for the production of a self-cleaning substrate surface according to the invention are preferably mixtures that include: structure forming particles and a coating or layer material. The particles preferably have an average particle diameter of less than 100 nm, and more preferably the particles have an average particle diameter in the range from 5 nm to less than 50 nm. As mentioned above, the particle diameter is that of the primary particles and the diameter of at least 90 %, and preferably substantially all of the particles, is preferably less than 100 nm, and more preferably less than 50 nm.

~~The layer-forming particulate or liquid material can be an organic or inorganic material. The term "layer-forming material" is understood as meaning a material which, in the context of application to the substrate by a physical or chemical route, is capable of forming a homogeneous layer and of fixing the structure-forming particles in the layer or/and on the substrate. If the material is an organic polymeric material or precursors of a polymer, this is present in the composition in the form of a solution in an organic or aqueous solvent or solvent mixture or in the form of an organic or aqueous suspension. The homogeneous layer is achieved by evaporation of the solvent and/or during a subsequent heat treatment by fusing together thermoplastic particles or by a condensation or polyaddition or polycondensation.~~

The coating, before application, can be in a particulate or liquid form. The coating or layer forming material can be an organic or inorganic material. The term "layer forming material" is a material that, in the context of application to the substrate by either a physical or a chemical route, is capable of forming a generally homogeneous layer and of fixing the structure forming particles in the layer or/and onto the substrate.

If the layer forming material is an organic polymeric material, or polymeric precursors, it is preferably in the form of a solution of an organic or aqueous solvent or solvent mixture or in the form of an organic or aqueous suspension. The applied coating or homogeneous layer is achieved by evaporation of the solvent, and then, during a subsequent heat treatment, by the fusing together of thermoplastic particles or by a condensation reaction, polycondensation reaction, or polyaddition reaction.

~~According to preferred embodiments of the composition, this comprises inorganic layer forming materials or at least precursors thereof. Particularly suitable layer forming organic materials are glass frits and oxidic raw materials (= precursors) which are capable of glass formation with other substances, such as, in particular, boric acid ( $B_2O_3$ ), bismuth oxide ( $Bi_2O_3$ ), alkali metal and alkaline earth metal oxides, zinc oxide and lead oxide as well as alkali metal silicates, and phosphates and borates. Most glass forming substances are contained in the composition in particulate form. Alkali metal oxides and alkali metal silicates are expediently contained in the composition in the form of aqueous alkali solution or in the form of water glass (sodium silicate solution).~~

If the layer forming material is an inorganic material, suitable layer forming inorganic materials include glass frits and oxidic raw materials (that is, glass precursors) which are capable of glass formation with other substances, such as, for example, boric acid ( $B_2O_3$ ), bismuth oxide ( $Bi_2O_3$ ), alkali metal and alkaline earth metal oxides, zinc oxide and lead oxide as well as alkali metal silicates, and phosphates and borates. Most of the glass forming substances in the composition are in particulate form. Alkali

metal oxides and alkali metal silicates in the composition are in the form of an aqueous alkali solution, or are in the form of water glass (sodium silicate solution).

~~According to a further alternative, the compositions according to the invention comprise an organometallic compound of one or more of the elements boron, silicon, aluminium, titanium and zirconium as the layer-forming material. The organometallic compounds are preferably those which contain alkoxy groups, acetyl groups or acetylacetonate groupings, so that Me-O-Me' structural elements are formed by a condensation reaction, wherein Me and Me' can be identical or different and represent the elements mentioned.~~

Alternatively, the layer forming material includes an organometallic compound of one or more of the elements boron, silicon, aluminium, titanium and zirconium as the layer forming material. The organometallic compound preferably contains alkoxy groups, acetyl groups or acetylacetonate group, so that Me-O-Me' structural elements are formed by a condensation reaction. The Me and Me' can be the same or different from each other and represent the elements mentioned. If a pulverulent composition is used, the pulverulent compositions can be applied to the substrate by dusting or by electrostatic coating.

~~The structure-forming particles and the layer-forming material are usually contained in the composition according to the invention in a weight ratio of 100 : 1 to 1 : 2; the weight ratio is preferably in the range from 20 : 1 to 1 : 1.~~

The composition that preferably includes the structure forming particles and the coating or layer forming material in a weight ratio of about 100 : 1 to about 1 : 2. Preferably, the weight ratio is in a range of from about 20 : 1 to about 1 : 1.

~~Pulverulent compositions according to the invention can be applied to the substrate by dusting or by electrostatic coating.~~

~~A preferred embodiment of the composition according to the invention also comprises, in addition to the layer forming materials and the structure forming particles, a liquid medium. The consistency of such a composition can be in wide ranges, for example for the purpose of application by spraying or dipping, a considerably lower viscosity is established than in the case of application of the composition by a conventional printing process. In the case of use of the composition by a printing process, for example a screen printing process, the consistency of the composition is preferably paste-like.~~

In addition to the layer forming materials and the structure forming particles, the composition according to the invention can also include a liquid medium. The consistency a composition that includes a liquid medium can be in a wide range of viscosities. For example, if the composition is applied by spraying or dipping, a considerably lower viscosity is established. But, if a conventional printing process is used to apply the composition a relatively higher viscosity can be used. For example, if a printing process, for example a screen-printing process, is used, the consistency of the composition is preferably paste-like.

The liquid medium can be an organic or organic aqueous or aqueous medium, which can comprise processing auxiliaries, such as agents to adjust the viscosity, in addition to obligatory components.

~~Particularly preferred compositions which are suitable for the formation of a structured surface of a substrate of glass, ceramic, metal or a glazed or enamelled substrate comprise, as the layer forming material, one or more glass frits as the main component, the softening point of these being sufficiently below the deformation temperature of the substrate to be coated. If the composition comprises raw materials which are capable of glass formation (= precursors), those substances which are capable of undergoing chemical bonding with one another and/or with structural elements of the substrate and/or structural elements of the nanoscale particles under conventional firing conditions are chosen. Boric acid and alkali metal phosphates are particularly suitable layer forming materials or precursors thereof.~~

A particularly preferred composition suitable for the formation of a structured surface of a glass, ceramic or metal substrate, or a glazed or enamelled substrate include (as the layer forming material) one or more glass frits as the main component. The softening point of the glass frits being sufficiently below the deformation temperature of the substrate. If the composition preferably further includes a raw material capable of glass formation (that is, a glass precursor). The raw material is selected based on the ability of the raw material to undergo chemical bonding under conventional firing conditions with itself, with structural elements of the substrate, and/or with structural elements of the nanoscale particles. For example, boric acid and alkali metal phosphates are particularly suitable layer forming materials or precursors thereof.

~~Using a liquid to paste like composition which comprises boric acid or an alkali metal dihydrogen phosphate as the layer forming material or precursor thereof and a pyrogenic oxide as the structure forming material, a firmly adhering structured surface can be formed on glass which, after hydrophobization with an organosilane, in particular a fluorine containing organosilane, leads to particularly good self-cleaning properties. The contact angle of a glass coated in this way is above 150°.~~

A preferred method according to the invention of firmly adhering to a glass structured surface includes using a liquid composition, or a paste-like composition, that includes boric acid or an alkali metal dihydrogen phosphate as the layer forming material, or a precursor thereof, and a pyrogenic oxide as the structure forming material. Subsequent to the formation of the structured surface, the surface is hydrophobized with an organosilane, preferably a fluorine containing organosilanes. The method results in a surface having particularly good self-cleaning properties. That is, the contact angle of a glass coated by this method is above 150°.

~~The liquid medium can be an organic or organic aqueous or aqueous medium, which can comprise processing auxiliaries, such as agents to adjust the viscosity, in addition to the obligatory components.~~

~~The surface of the micro-rough layer is at least partly hydrophobized, in particular the peaks and elevations. Preferably, however, the entire surface is hydrophobized. The hydrophobization substantially comprises a very thin coating, for example of a thickness of 1 to 10 nm, which adheres firmly to the underlying surface. This adhesion is effected by film formation of the coating composition after application. Preferred hydrophobizing agents are bonded chemically to the substrate, for example via an Si-O-Si bridge. Such~~

~~bridges result from the reaction of a silanol group of a silicatic material of the structured coating with an alkoxysilane or alkoxysiloxane. Preferred substrates according to the invention with a self-cleaning surface have a coating, often only a few atom layers thick, based on an alkyltrialkoxysilane and preferably a longer chain fluoroalkyltrialkoxysilane or oligomers of these silanes.~~

With further reference to the coating or layer forming material, the surface of the micro rough layer is at least partly hydrophobized, and preferably at least the peaks and elevations are hydrophobized. Preferably, however, the entire surface is hydrophobized. The hydrophobization includes the application of a very thin coating, which adheres firmly to the underlying surface. The thin coating has, for example, of a thickness of 1 nm to 10 nm. The adhesion is preferably caused by the coating composition's film formation after application. Preferred hydrophobizing agents chemically bond to the substrate to form, for example, an Si-O-Si bridge. Such bridges result from the reaction of a silanol group of a silicatic material of the structured coating with an alkoxysilane or alkoxysiloxane. An exemplary preferred substrate with a self-cleaning surface according to the invention has a coating only a few atom layers thick. The coating is based on an alkyltrialkoxysilane, and preferably a longer chain fluoroalkyltrialkoxysilane, or an oligomer thereof.

~~The substrates according to the invention with a self-cleaning surface can be produced in a simple manner by a process which comprises the following steps:~~

The substrates according to the invention with a self-cleaning surface can be produced by a process that includes the following steps:

~~1. coating of a surface of the substrate with a composition comprising structure-forming particles and an inorganic or organic layer-forming material, this composition being pulverulent or, preferably, liquid to paste-like,~~

1. coating of a surface of the substrate with a composition, the composition including structure forming particles and an inorganic or organic layer forming material, the composition is pulverulent or, preferably, has a liquid to paste-like consistency,

~~2. formation of a cohesive layer which fixes the structure-forming particles and adheres firmly to the substrate and~~

2. forming a cohesive layer that fixes the structure forming particles and adheres the structure forming particles firmly to the substrate to form a structured surface; and

~~3. hydrophobization of the structured surface with a hydrophobizing agent, in particular an organosilane, which adheres firmly to the structured surface or forms a chemical compound with this.~~

3. hydrophobizing the structured surface with a hydrophobizing agent, preferably an organosilane, which adheres firmly to the structured surface, or forms a chemical bond thereto.

~~A particular feature of the process is the use of structure-forming particles with an average diameter of less than 100 nm, preferably less than 50 nm, and at least 5 nm. The profile heights of the elevations are, if no particles in the  $\mu\text{m}$  range which form an over structure are present, less than 100 nm, in particular less than 50 nm. The structure-forming particles and the layer-forming materials are those which have already been mentioned above.~~



A particular feature of the process is the use of structure forming nanoscale particles with an average diameter of less than 100 nm, preferably less than 50 nm, but at least 5 nm. The profile heights of the elevations are less than 100 nm, and preferably less than 50 nm. If microscale particles in the  $\mu\text{m}$  range that form an over structure are present, then the nanoscale particles are arranged on the microscale particles.

~~The compositions to be applied by means of a conventional coating process preferably comprise the constituents essential to the invention, that is to say the structure forming particles and the layer forming material, in a ratio of amounts which has already been mentioned above. If a pulverulent composition is used for the coating, this can be carried out by dusting the substrate or by electrostatic coating. The coating is preferably carried out using a liquid to paste like composition, the liquid media contained in such a composition being those systems such as are known to the expert, in particular the decoration expert in the glass and ceramics industry. The coating with a liquid to paste like composition can be carried out by spraying, brushing, pouring or dipping or by means of a conventional printing process, such as a screen printing or a dabber transfer printing process.~~

A conventional coating process type composition includes the structure forming particles and the layer forming material and is applied by conventional coating processes. A pulverulent coating type composition is applied to the substrate surface by dusting the substrate or by electrostatic coating. A printing coating type composition preferably has a liquid to paste-like composition and is preferably applied to the substrate surface by spraying, brushing, pouring, dipping or by another conventional printing process, such as a screen printing or a dabber transfer printing process.

~~The feature "formation of a cohesive layer which adheres firmly to the substrate and fixes the structure forming particles" can vary according to the substrate to be coated and the composition of the coating composition. If the composition comprises an organic polymeric material which is pulverulent or suspended in a liquid medium, a cohesive layer can be produced by passing the coated substrate to a heat treatment, solvent optionally present evaporating and polymer particles fusing together or, in the case of multi-component systems, reacting to give a polymeric material.~~

The "formation of a cohesive layer which adheres firmly to the substrate and fixes the structure forming particles" can vary based on the substrate to be coated and by the coating composition and type. A cohesive layer can be produced by passing a coated substrate to a heat treatment if the composition includes an organic polymeric material that is either pulverulent or suspended in a liquid medium. The solvent, if present, evaporates, and polymer particles fuse together. Or, in the case of multi component systems, precursors react to form a polymeric material that binds the structure forming particles to the substrate surface.

~~Compositions which are applied to a substrate which can undergo firing, that is to say a glass, ceramic or metal substrate or a glazed or enamelled substrate, and comprise a glass frit or constituents which are capable of glass formation with the substrate surface and/or the particles, can be converted into a cohesive structured layer by a heat treatment, that is to say in this case firing. During firing, the glass frit melts to a homogeneous layer; the constituents of the composition which are capable of glass formation form [sic] a chemical reaction with reactive groups of the substrate and/or the structure forming particles to form vitreous structures with structural elements of the~~

~~formula Me-O-Me', wherein Me and Me' have the meaning already given. The glass frits and/or constituents capable of glass formation contained in the composition are chosen such that the heat treatment, that is to say the firing, can be carried out at a temperature below the deformation temperature of the substrate. In the coating of glass, the composition will accordingly comprise those layer forming constituents which melt below 650 °C, in particular in the range from 450 to 600 °C and can form the required structures.~~

Some compositions according to the invention can be converted into a cohesive structured layer by a heat treatment or a firing process. The proviso is that the substrate must be able to withstand the heat treatment or firing process. Suitable substrates include glass, ceramic, or metal substrates or glazed or enamelled substrates. The compositions that can so convert include glass frit or constituents that are capable of glass formation with the substrate surface and/or the particles.

During the firing process, the glass frit melts to form a homogeneous molten layer. The composition that is capable of glass formation, undergoes a chemical reaction with reactive groups of the substrate and/or the structure forming particles to form a vitreous structure having structural elements of the formula Me-O-Me'. The glass frits and/or constituents capable of glass formation contained in the composition are selected such that the heat treatment is performed at a temperature below the deformation temperature of the substrate. In the coating of glass, the composition will accordingly comprise those layer-forming constituents that melt below about 650 °C, and preferably melt in the range of from about 450 to about 600 °C, and can form the required structures.

~~The nanostructured coating to be applied to the substrate can have a varying layer thickness. Preferably, the layer thickness of layers which comprise as structure-forming particles exclusively particles according to the invention with an average diameter of less than 100 nm, in particular less than 50 nm, and at least 5 nm is in the range from 5 to 1000 nm. If the composition additionally comprises larger structure-forming particles, for example particles with a diameter in the range from 0.5 to 15  $\mu\text{m}$ , the maximum height of the layer is of course higher. In the case mentioned last, the nanoscale structure according to the invention is on a micro-rough over-structure. Alternatively, it is also possible for a substrate with a micro-rough surface structure, for example a surface structure such as substrates according to DE Patent Application 100 16 485.4 have, already to be coated with a composition according to the invention which comprises as structure-forming particles substantially only particles with a particle diameter of less than 100 nm, preferably less than 50 nm, to be baked and then to be hydrophobized.~~

A nanostructured coating according to the invention can have a varying layer thickness. Preferably, the layer thickness is in the range of from about 5 nm to 1000 nm. If the coating additionally includes the larger particles (to form the microscale overstructure), the maximum height of the layer higher. Alternatively, a substrate already coated with a composition that forms a micro rough surface structure, preferably includes a coating using only nanoscale particles having a particle diameter of less than 100 nm, preferably less than 50 nm. After the nanoscale coating is applied the substrate can be baked and hydrophobized.

~~After the formation of the structured surface, the hydrophobization stage follows:~~

After the formation of the structured surface, the hydrophobization stage follows:

~~The hydrophobization can be carried out by application of a hydrophobic lacquer or by polymerization of monomers on the micro rough surface. Suitable polymeric lacquers are solutions or dispersions of e.g. polyvinylidene fluoride. A hydrophobization can also be carried out by plasma polymerization of completely or partly fluorinated vinyl compounds.~~

The hydrophobization can be carried out by application of a hydrophobic lacquer or by polymerization of monomers on the micro rough surface. Suitable polymeric lacquers are solutions or dispersions of e.g. polyvinylidene fluoride. A hydrophobization can also be carried out by plasma polymerization of completely or partly fluorinated vinyl compounds.

~~The hydrophobization is particularly expediently carried out using reactive alkyl or, preferably, fluoroalkylsilanes and oligomeric alkyl or fluoroalkylsiloxanes. The silanes or siloxanes preferably contain one or more alkoxy or acetyl groups, such as ethoxy groups, as the reactive group. Crosslinking of the hydrophobizing agent and also chemical bonding thereof to a silicatic surface containing silanol groups is possible by means of these functional groups. Silanizing agents which are particularly preferably to be used are tridecafluorooctyltriethoxysilane and oligomers thereof. Such products can be applied to the surface to be hydrophobized in the form of dilute organic, in particular alcoholic, aqueous organic and aqueous solutions, for example by dipping, spraying or brushing.~~

The hydrophobization is carried out using reactive alkyl or, preferably, fluoroalkylsilanes and oligomeric alkyl or fluoroalkylsiloxanes. The silanes or siloxanes

preferably contain one or more alkoxy or acetyl groups, such as ethoxy groups, as the reactive group. Crosslinking of the hydrophobizing agent and also chemical bonding thereof to a silicatic surface containing silanol groups is possible by means of these functional groups. Preferable silanizing agents include tridecafluorooctyltriethoxysilane and oligomers thereof. Such products can be applied to the surface to be hydrophobized by, for example, dipping, spraying or brushing in or with a dilute organic solution, preferably an alcoholic solution, or an aqueous organic solution or an aqueous solution.

~~After application of a solution comprising a fluorine containing silane or siloxane to the substrate, the substrate is dried and cured, preferably at a temperature of up to 500 °C, for example for 30-60 min at about 150 °C, 10-15 min at 250 to 300 °C or 1 min at about 500 °C. The optimum of the after treatment with heat in respect of highest abrasion resistance is at a temperature in the range from 200 to 300 °C.~~

After applying a solution that includes a fluorine containing silane or siloxane to the substrate, the substrate is dried and cured. The drying and curing is preferably at a temperature of up to about 500 °C. The dry or cure time is, for example, 30 to about 60 min at about 150 °C, 10 to 15 min at 250 to 300 °C, and about 1 minute at about 500 °C. The optimum heat treatment to elicit the highest abrasion resistance is at a temperature in the range from 200 to 300 °C.

~~Using dilute solutions of the silanes or siloxanes mentioned, layers a few nm thick which have a very high chemical and mechanical resistance and are 2- and 3-dimensional siloxane networks are obtained.~~

~~The hydrophobic layers accessible using reactive fluoroalkylsilanes or siloxanes are distinguished by a similarly good hydrophobicity and oleophobicity, so that substrates according to the invention contaminated with hydrophobic dirt particles can also easily be cleaned with water.~~

Using dilute solutions of the silanes or siloxanes mentioned, layers a few nm thick that have a very high chemical and mechanical resistance and are 2 and 3 dimensional siloxane networks are obtained. The hydrophobic layers accessible using reactive fluoroalkylsilanes or -siloxanes are distinguished by a similarly good hydrophobicity and oleophobicity, so that substrates according to the invention contaminated with hydrophobic dirt particles can also easily be cleaned with water.

~~The invention also relates to the use of a substrate according to the invention with a self-cleaning surface. Examples are glass panes for vehicles and windows, construction glass, ceramic tiles, roof tiles, covers on photovoltaic solar cells, metal profiles and lacquered substrates, such as car lacquers.~~

The invention also relates to the use of a substrate with a self-cleaning surface. Examples of such uses include glass panes for vehicles and windows, construction glass, ceramic tiles, roof tiles, covers on photovoltaic solar cells, metal profiles and lacquered substrates, such as car lacquers.

~~The substrates according to the invention with a self-cleaning surface are distinguished by a very high efficiency of the self-cleaning property. The contact angle of preferred substrates according to the invention with respect to water is in general about and often above 150°.~~

~~A particularly outstanding feature of substrates according to the invention is the transparency of the nanostructured coating. Transparent substrates of plastic and glass and glazed or enamelled substrates are accordingly particularly suitable for being provided with a transparent coating according to the invention and therefore for obtaining high quality self-cleaning surfaces which are themselves transparent and therefore also clearly reveal underlying decorations.~~

A particularly outstanding feature of substrates according to the invention is the transparency of the nanostructured coating. Transparent substrates of plastic and glass, and of glazed or enamelled substrates are suitable for use as a transparent coating and therefore useful for surfaces of substrates that are themselves transparent, or are decorated, and to thus reveal underlying decorations. Advantages of compositions according to the invention include easy accessibility and range of composition variation. The compositions are useful to coat diverse substrates and still produce good self-cleaning properties.

~~Essential advantages of compositions according to the invention are their easy accessibility and range of variation in respect of composition. The compositions can therefore be used for coating the most diverse substrates and producing good self-cleaning properties.~~

~~The stages of the process according to the invention are based closely on those process stages such as are used, for example, for decoration purposes in the glass and ceramics industry, but are also conventional in the lacquering of metallic substrates with stoving lacquers. The devices and technologies known to the expert can therefore be used.~~



The stages of the process according to the invention are based closely on those process stages such as are used, for example, for decoration purposes in the glass and ceramics industry, but are also conventional in the lacquering of metallic substrates with stoving lacquers. The devices and technologies known to the expert can therefore be used.

#### Examples

#### EXAMPLES

~~1. Production of float glass or high grade steel with a transparent self-cleaning surface~~

EXAMPLE 1 - Production of float glass or high grade steel with a transparent self-cleaning surface.

~~4 mm float glass was coated with a composition according to the invention by means of screen printing. The composition comprised 0.5 wt.% boric acid ( $B_2O_3$ ) and 4 wt.% pyrogenic silica in a screen printing medium (no. 80858 from dmc<sup>2</sup> AG). The pyrogenic silica had an average diameter of the primary particles of 12 nm. The printing medium was a water friendly medium. The screen printing was carried out using a 100 T screen. After drying, the coating was shock fired at 660°C in the course of 4 min. The hydrophobization of the structured stoved surface was carried out using a fluoroalkylsilane formulation, that is to say an ethanolic solution of tridecafluorooctyltriethoxysilane. The solution was introduced over the surface, and curing was then carried out at elevated temperature.~~

~~The float glass coated in this way was transparent and had a contact angle of above 150°.~~

A 4 millimeter (mm) float glass was coated with a composition according to the invention by means of a screen printing process. The composition included 0.5 wt.% boric acid ( $B_2O_3$ ) and 4 wt.% pyrogenic silica in a screen printing medium (no. 80858, commercially available from dmc<sup>2</sup> AG (Germany)). The printing medium was a water friendly medium. The pyrogenic silica had an average diameter of the primary particles of 12 nm. The screen printing was carried out using a 100 T screen. After drying, the coating was shock fired at 660 °C in the course of 4 min. The hydrophobization of the structured stoved surface was carried out using a fluoroalkylsilane formulation, that is to say an ethanolic solution of tridecafluorooctyltriethoxysilane. The solution was introduced over the surface, and curing was then carried out at elevated temperature. The float glass coated in this way was transparent and had a contact angle of above 150°.

~~2.Example 1 was repeated with the only difference that the composition comprised 0.5 wt.% diammonium hydrogen phosphate ( $(NH)_2HPO_4$ ) [sic] instead of boric acid as the layer forming material. After the hydrophobization, the glass coating showed outstanding self-cleaning properties.~~

EXAMPLE 2 - Production of float glass or high grade steel with a transparent self-cleaning surface.

The method used was the same as described in EXAMPLE 1, except that the composition comprised 0.5 wt.% diammonium hydrogen phosphate ( $(NH)_2HPO_4$ ) instead of boric acid as the layer forming material. After the hydrophobization, the glass coating showed outstanding self-cleaning properties.

~~It is assumed that during firing vitreous structures with the structural element Si-O-B or Si-O-P or metal-O-P form between the boric acid or the phosphate and reactive centres of the glass or metal and the structure forming silica particles.~~

It is assumed that during firing vitreous structures with the structural element Si-O-B or Si-O-P or metal-O-P form between the boric acid or the phosphate and reactive centres of the glass or metal and the structure forming silica particles.

~~Substrate was degreased V4A high grade steel. A composition with 4 wt.% pyrogenic silica ( $d = 12$  nm) and diammonium hydrogen phosphate in an amount of (a) 0.25 wt.%, (b) 0.5 wt.% and (c) 1.0 wt.% in screen printing medium 80858 was used for the coating. After coating by means of screen printing, firing was carried out for 6 minutes at 660 °C. A scratch resistant self-cleaning surface was obtained in all three cases.~~

EXAMPLE 3 - Production of a metal substrate having a self-cleaning surface.

The substrate was degreased V4A high grade steel. A composition with 4 wt.% pyrogenic silica (having a diameter of 12 nm) and diammonium hydrogen phosphate in an amount of (a) 0.25 wt.%, (b) 0.5 wt.% and (c) 1.0 wt.% in screen printing medium 80858 was used for the coating. After coating by means of screen printing, firing was carried out for 6 minutes at 660 °C. A scratch resistant self-cleaning surface was obtained in EXAMPLES 1-3.

What is claimed is:

~~1.A substrate, in particular a substrate with at least one self-cleaning surface, the substrate comprising a coating of glass, ceramic, plastic and metal, or a glazed or enamelled substrate, where the coating comprises particles which form a surface structure that is at least partly superficially hydrophobic, wherein, the structure-forming particles have an average diameter of less than 100 nm.~~

~~2.A substrate with a self-cleaning surface as defined in claim 1, wherein the structure-forming particles have an average diameter of less than 50 nm and at least 5 nm.~~

~~3.A substrate with a self-cleaning surface as defined in claim 1, wherein the structure-forming particles are chosen from the series consisting of metal oxides, mixed oxides, silicates, sulfates, phosphates, borates, carbon blacks, metal powders, metal sulfides, selenides, sulfoselenides and oxosulfides, metal nitrides and oxide-nitrides and organic polymers.~~

~~4.A substrate with a self-cleaning surface as defined in claim 1, wherein the structure-forming particles are metal oxides from the series consisting of  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{SnO}_2$ , in particular pyrogenically prepared oxides thereof.~~

~~5.A substrate with a self-cleaning surface as defined in claim 1, wherein the coating comprises the structure-forming particles bonded in or by means of an inorganic or organic layer-forming material.~~

~~6.A substrate with a self-cleaning surface as defined in claim 5, where the layer-forming material is a glass or a material which forms Me-O-Me' structural~~

elements, wherein Me and Me' are identical or different and represent B, Si, Al, P, Ti, Sn or Zr.

~~7. A substrate with a self-cleaning surface as defined in claim 5, where in addition to the structure forming particles with an average diameter of less than 100 nm, in particular less than 50 nm, the layer according to the invention or a layer applied underneath with a micro-scale surface structure also comprises particles which form an over-structure and have an average diameter of 0.1 to 50  $\mu\text{m}$ , in particular 0.5 to 15  $\mu\text{m}$ .~~

~~8. A substrate with a self-cleaning surface as defined in claim 5, where the coating comprises structure-forming particles with an average diameter of less than 100 nm, in particular less than 50 nm, and one or more layer-forming inorganic or organic materials in a weight ratio in the range from 100 : 1 to 1 : 2, in particular 20 : 1 to 1 : 1.~~

~~9. A substrate with a self-cleaning surface as defined in claim 1, where the substrate is glass or a plastic or an enamelled or glazed substrate.~~

~~10. A substrate as defined in claim 9, where the substrate is glass and the substrate coated according to the invention is substantially transparent.~~

~~11. A composition for the production of a substrate with at least one self-cleaning surface as defined in claim 1, where the composition comprises structure-forming particles with a particle diameter of less than 100 nm, in particular less than 50 nm, and at least 5 nm, and a layer-forming particulate or liquid material in a weight ratio of 100 : 1 to 1 : 2.~~

~~12. A composition as defined in claim 11, where the layer-forming material comprises as the main component one or more glass frits or/and one or more glass raw materials which, during firing, form a glass or vitreous structures with one another~~

~~or/and with groups of the substrate or/and of the structure forming particles which are capable of glass formation.~~

~~13.A composition as defined in claim 12, where the composition substantially comprises structure forming particles and a layer forming material, in particular, a particulate material which can be suspended in a liquid medium.~~

~~14.A composition as defined in claim 11, where the composition comprises structure forming particles according to the invention with a particle diameter of less than 50 nm and at least 5 nm, in particular a silica, and, as the layer forming material, one or more oxides from the series consisting of  $B_2O_3$ ,  $Bi_2O_3$ , alkali metal oxides, zinc oxides and lead oxides or borates, silicates or phosphates or a glass frit which melts below 650 °C.~~

~~15.A composition as defined in claim 14, where the composition substantially comprises 1 to 10 wt.% pyrogenic silica ( $SiO_2$ ) and 0.1 to 2 wt.% boric acid ( $B_2O_3$ ), alkali metal or ammonium dihydrogen phosphate or di-alkali metal or diammonium hydrogen phosphate or a glass frit which melts below 600 °C, in each case based on the composition, and a printing medium.~~

~~16.A process for the production of a substrate with at least one self-cleaning surface as defined in claim 1, comprising (i) coating of a surface of the substrate with a composition comprising structure forming particles and an inorganic or organic layer-forming material, (ii) formation of a cohesive layer which fixes the structure forming particles and adheres firmly to the substrate and (iii) hydrophobization of the structured surface formed, where the structure forming particles have an average diameter of less than 10 nm, preferably less than 50 nm, and at least 5 nm.~~

~~17. A process as defined in claim 16, where a substrate from the series consisting of glass, ceramic, plastic and metal or a glazed or enamelled substrates, which can already have a micro-rough surface, is coated with a composition according to claim 11, which comprises a glass frit or a glass-forming raw material, the coated substrate is subjected to firing suitable for the formation of a firmly adhering cohesive layer, and the structured surface contained is coated with an organosilane, in particular fluoroorganosilane, and thereby hydrophobized.~~

~~18. A process as defined in claim 16, where the composition used to form the surface structure is applied in a liquid to paste-like consistency by means of a printing process, by spraying, brushing, pouring or dipping.~~

~~19. The use of a substrate with a self-cleaning surface as defined in claim 1 for the production of glass panes for vehicles and windows, construction glass, ceramic tiles, roof tiles, covers on photovoltaic solar cells, metal profiles and lacquered substrates.~~

~~Substrates with a self-cleaning surface, a process for their production and their use~~

Abstract ABSTRACT OF THE INVENTION

~~Substrates, in particular a~~ A substrate of glass, ceramic, plastic and metal and glazed or enamelled substrates, with a self-cleaning surface comprise an at least partly superficially hydrophobic structured (elevations and depressions) coating located on the substrate. metal, or a glazed or enamelled substrate, with a self-cleaning and/or hydrophobic surface. The substrate having disposed thereon a coating that includes a plurality of particles affixed to the surface of the substrate by a binder. The particles are preferably of nanoscale size and extend outwardly from a surface of the coating to form a nano-rough surface. The nano-rough surface causes a hydrophobic or water repellent effect. The binder can be formed from an organic or an inorganic material and operates to fix the plurality of particles to substrate surface.

~~Substrates according to the invention comprise particles with an average diameter of less than 100 nm, in particular 5 to less than 50 nm, for formation of the structure of the coating.~~

~~Compositions according to the invention which are employed for the production of the structured coating of substrates according to the invention comprise, in addition to the structure-forming particles, a layer-forming material in a weight ratio of 100 : 1 to 1 : 2, in particular 20 : 1 to 1 : 1.~~

~~In addition to having good self-cleaning properties, the coating is distinguished by its transparency. The use of the substrates is aimed in particular at the most diverse glass articles.~~